Effect of Processing on Flavor Precursor Amino Acids and Volatiles of Sesame Paste (Tehina)

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ABSTRACT: The content of flavor precursor free amino acids in dehulled sesame seeds, subjected to roasting (R), steaming (S), roasting plus steaming (RS) and microwaving (M), was determined and compared with those of the raw (RW) seeds. R, RS, and S had major effects in reducing the content of free amino acids from 2360 μg/g to 582, 795 and 884 μg/g, respectively; M had no effect on the content of free amino acids. Meanwhile, flavor volatiles of the raw and processed seeds were compared by means of a dynamic headspace analyzer/gas chromatograph–mass spectrometer. Volatiles of RW seeds contained 85 compounds, whereas under the analytical conditions employed, seeds subjected to R, RS, S, and M had 117, 97, 93 and 87 compounds, respectively. Among volatiles identified in the RW seeds were 36 hydrocarbons, 8 aldehydes, 4 ketones, 8 alcohols, 2 acids, 2 esters, and 1 pyrazine. The only pyrazine identified in the RW seeds was 2,5-dimethylpyrazine. Pyrazines, generally recognized as contributors to the roasted aroma of foods, were more numerous (10 in R, 6 in RS, 2 in S, and 2 in M) and prevalent (8.71% in R, 2.97% in RS, 2.04% in S, 0.53% in M, and 0.25% in RW) in the volatiles of processed sesame seeds. The chemical nature of pyrazines also depended on the process employed. Multivariant analysis indicated a highly negative correlation between the loss of free amino acids and production of volatile flavor compounds in the R and RS samples, while the M sample remained unchanged. Furthermore, both R and RS seeds contained dimethyl sulfide and dimethyl disulfide, whereas no sulfur-containing compounds were present in other samples. Of the processed seeds, the flavors of R and RS samples were considered as acceptable, and the flavor intensity of the former was deemed stronger than that of the latter by the experimenters.

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KEY WORDS: Flavor, free amino acids, microwaving, processing, roasting, sesame seeds, steaming, tehina, volatiles.

Roasted sesame seeds are widely used in the East Asian and Middle Eastern countries. The roasting process renders a unique nutty flavor to the seeds (1). Roasting is the key step in processing sesame because color, composition, and quality of the resultant oils are influenced by roasting conditions (2,3).

Takei *et al.* (4) have reported that acetylpyrazine has a strong popcorn-like aroma, which apparently plays an important role in the characterization of the flavor of sesame oil. Moreover, Kinoshita and Yamanishi (5) and Manley *et al.* (1) have investigated the heterocyclic aroma compounds of roasted sesame seeds and reported them to be mainly alkylpyrazine derivatives. On the other hand, Soliman *et al.* (6) have identified *n*-octanol and 2-furfuryl alcohol in the flavor volatiles of roasted sesame seeds and claimed them to be the source of the roasted aroma in the seeds. Recently, Schieberle (7) reported that 2-acetyl-1-pyrroline, 2-furfurylthiol, 2-phenylethylthiol, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone were important contributors to the overall roasty and sulfury odor of mildly roasted sesame.

Lee *et al.* (8) reported volatile compounds of sesame seeds roasted at different temperatures. Certain volatile compounds that contribute to desirable flavor characteristics of foods, such as cheese, cream, heated butter and peas, were present (9). The compounds responsible for these flavors are usually a complex mixture with varying molecular weight and polarity components and contain alkanes, alkenes, alkanals, alkenals, alkadienals, substituted furans, alkanones, alkenones, alkanols, alkenols, and heterocyclic compounds (9).

Determination of the flavor impact components in heated foods is difficult due to the large number of compounds present and their different flavor threshold values (10). However, isolation and identification of flavor chemicals, formed in food under various heating conditions, is one avenue to understand the formation of complex flavor compounds in roasted foods. Recently, dynamic headspace analysis/gas chromatography–mass spectrometry (DHA/GS–MS) has gained popularity as an effective and sensitive technique for analysis of flavor volatiles of food products. Its excellent purging process increases the sensitivity of the method. This method provides a sensitive means for detecting low levels of oxidative deterioration products in a variety of lipid-containing foods (11). Furthermore, aroma extract dilution analysis (AEDA) has recently been used to identify the key odorants in different food products, including roasted sesame (7).

Yoshida (12) reported that sesame oil prepared by roasting at 180°C had the best flavor score. However, little is known about how microwave and other modified roasting conditions affect the flavor components of sesame seeds. We have previously reported the effect of processing of sesame on the oxidative stability of oils extracted from coated and dehulled

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seeds (13) and examined the content of endogenous antioxidants as affected by processing (14). The present study reports changes in the content of free amino acids, which are known precursors of Maillard reaction products, and formation of heterocyclic flavor compounds as well as the effect of processing on the chemical nature of volatile components of freshly prepared pastes from raw (RW) sesame seeds and seeds exposed to various treatments of roasting (R), steaming (S), roasting plus steaming (RS), and microwaving (M). We did not intend to identify important flavor-impact compounds in processed seeds as recently described by Schieberle (7).

MATERIALS AND METHODS

Materials. Dehulled seeds from *S. indicum* L. (Giza 24, Egyptian variety) were obtained from Sacs Company (Alexandria, Egypt). All chemicals used were acquired from Sigma (St. Louis, MO) or Aldrich Chemical Company (Milwaukee, WI).

Sample preparation. Seeds used were RW, R at 200°C for 20 min, S at 100°C for 20 min, R at 200°C for 15 min and then S for 7 min, or M at 2450 MHz for 15 min. Each sample was ground in a coffee grinder for 10 s, followed by a quiescent period of 2 min. This process was repeated eight times for preparation of the paste, known as tehina, and its subsequent use for analysis. For processed seeds, grinding was carried out 6 h post-processing.

Determination of free amino acids. The content of free amino acids in sesame pastes was determined by homogenizing (Polytron homogenizer, Model PT3000, Kinematica AG, Switzerland; speed 4) 2.0 g of the sample with 20 mL of ice-cold 6% (wt/vol) perchloric acid. After 30 min incubation at 0°C, samples were centrifuged at 3000 × *g* for 10 min at 5°C. The procedure was repeated twice, and the pH of the combined supernatants was adjusted to 7.0 with a 33% (wt/vol) KOH solution. Perchlorate precipitates were recovered after centrifugation at 3000 × *g* for 10 min. The supernatant was acidified to pH 2.2 with 10 M HCl, diluted at a ratio of 1:1.5 (vol/vol) with a 1.0% (wt/vol) lithium citrate buffer, pH 2.2. The content of free amino acids was then determined in a Beckman 121 MB amino acid analyzer (Beckman Instruments, Palo Alto, CA) (15).

DHA/GC analysis. The headspace volatile compounds of sesame paste after different treatments were isolated by a DHA, Tekmar LSC 2000 (Tekmar, Inc., Cincinnati, OH). Sesame paste (1 g) was immediately transferred into a 25-mL Tekmar sample purger. Samples were heated at 45°C for 1 min in the sample heater and then purged with high-purity helium at 40 mL/min for 1 h to isolate headspace volatiles, which were adsorbed on approximately 150 mg of Tenax^{TA} (Tenax^{TA}, 2,6-diphenyl-*p*-phenylene oxide polymer; Tekmar, Inc.) in a trap column. It was also dry-purged for 30 min. The adsorbed volatile compounds in the Tenax column were thermally desorbed at 220°C for 8 min with nitrogen gas at 1 mL/min. Desorbed compounds were cyrofocused at the capillary interface, maintained at −120°C with liquid nitrogen. All condensed volatile compounds in the capillary interface were then automatically injected onto the GC column at 220°C for 2 min.

GC (HP 5980; Hewlett-Packard, Avondale, PA) was used with a fused-silica capillary column (DB-Wax; 60 m × 0.25 mm i.d. × 0.25 μm film thickness; J & W Scientific, Folsom, CA) and a flame-ionization detector. Ultra high-purity helium was used as a carrier gas at a flow rate of 0.9 mL/min. The oven temperature was increased from 50 to 210°C at 3°C/min, then held at 210°C for 15 min. The GC peak areas of the volatile compounds were calculated by an electronic integrator (HP3390A; Hewlett Packard).

Identification of volatile compounds. MS data of volatile compounds were obtained by a combination of DHA, GC, and MS (HP5971; Hewlett-Packard). A fused-silica capillary column (DB-Wax; 60 m × 0.25 mm i.d. × 0.25 μm film thickness; J & W Scientific) and ultra high-purity helium at a flow rate of 0.9 mL/min were used. MS conditions were: ionization voltage 70 eV; ion source temperature at 180°C, mass scan range 25–300 *m/z*. The mass spectra of volatile compounds were tentatively identified by comparison with reference spectra of NBS54K and OG1 mass spectra database (Ogawa & Co., Ltd., Tokyo, Japan). Compounds were confirmed by comparing their mass spectra and GC retention times to those of standard compounds.

Multivariate analysis. Factor analysis and cluster analysis were performed with SPSS 6.1 for windows (SPSS Inc., Chicago, IL) on an IBM AT compatible personal computer. Prior to the factor analysis, data matrices of free amino acids and volatiles were combined to examine the relations between the depletion of free amino acids and formation of volatiles due to heat treatments. However, volatiles that appeared only in one sample were removed from the data matrix because such variables cannot be handled statistically in the factor analysis. In cluster analysis, distances among samples were calculated first based on their Euclean distances, and the resulting clusters were merged by Ward's method.

RESULTS AND DISCUSSION

Table 1 summarizes the content of free amino acids in the RW sesame seeds, subjected to different treatments of R, S, RS, and M. The effect of processing on reducing the content of free amino acids was in the decreasing order of RW ≈ M > S > RS > R. Thus, roasting had a maximum effect on reducing the content of free amino acids, while microwave heating had no effect. Free amino acids are known to undergo condensation reactions with reducing sugars present and, under appropriate moisture and heating conditions, produce Maillard reaction products, which would then form a number of volatile heterocyclic compounds, including pyrazines (3). In this work, we did not intend to explore the identity of flavor-impact compounds in processed sesame products as described recently by Schieberle (7), but we wanted to observe changes in volatile components as affected by processing. The total ion chromatograms of flavor volatiles of the raw and processed sesame seeds (Fig. 1) show that there were a myr-

TABLE 1
Effect of Processing on the Content (μg/g) of Free Amino Acids in Dehulled Sesame Seed Pastes Prepared from Raw (RW); Microwaved (M), Steamed (S), Roasted Plus Steamed (RS), and Roasted (R) Seeds[a]

Amino acid	RW	R	S	RS	M
Alanine	140 ± 5.4	48 ± 2.5	57 ± 2.2	50 ± 3.0	136 ± 3.8
Arginine	249 ± 6.8	74 ± 2.4	109 ± 3.9	82 ± 4.0	254 ± 7.2
γ-Aminobutyric acid	123 ± 8.1	35 ± 2.0	36 ± 2.0	37 ± 1.9	131 ± 5.9
Asparagine	281 ± 8.5	65 ± 1.8	92 ± 2.9	70 ± 3.0	257 ± 9.1
Aspartic acid	94 ± 4.8	33 ± 2.6	44 ± 2.8	37 ± 1.5	99 ± 3.2
Cysteine	19 ± 1.2	trace	5 ± 0.6	2.1 ± 0.5	21 ± 1.0
Glutamic acid	366 ± 9.9	49 ± 2.8	90 ± 3.4	58 ± 4.0	338 ± 10.2
Glutamine	80 ± 4.7	2 ± 0.1	23 ± 1.6	3 ± 0.6	91 ± 2.0
Glycine	54 ± 4.0	36 ± 1.6	38 ± 2.0	38 ± 1.3	70 ± 1.9
Histidine	49 ± 2.0	12 ± 2.0	20 ± 1.8	12 ± 1.1	48 ± 2.6
Isoleucine	69 ± 3.8	16 ± 1.1	37 ± 2.0	23 ± 0.9	78 ± 1.7
Leucine	102 ± 6.7	20 ± 0.8	42 ± 2.8	25 ± 1.6	116 ± 4.6
Lysine	64 ± 6.1	22 ± 1.8	32 ± 1.7	29 ± 2.1	77 ± 6.0
Methionine	31 ± 2.4	7 ± 0.8	10 ± 1.0	9 ± 0.6	36 ± 16
Phenylalanine	181 ± 9.2	28 ± 1.3	48 ± 3.0	36 ± 2.8	180 ± 6.2
Proline	47 ± 5.0	17 ± 1.4	28 ± 3.0	18 ± 1.5	57 ± 2.5
Serine	72 ± 3.1	28 ± 2.1	38 ± 2.0	37 ± 3.1	74 ± 2.6
Threonine	70 ± 4.2	18 ± 0.9	37 ± 1.8	22 ± 2.1	71 ± 3.0
Tryptophan	94 ± 5.6	6 ± 0.4	13 ± 1.1	6 ± 0.3	91 ± 4.6
Tyrosine	91 ± 4.9	18 ± 0.9	34 ± 2.6	20 ± 1.9	91 ± 3.1
Valine	84 ± 3.2	18 ± 1.1	41 ± 2.8	29 ± 1.7	98 ± 2.9
Total	2360 ± 110.6	582 ± 31.4	884 ± 48.1	795 ± 37.5	2374 ± 85.7

[a] Results are mean values of three determinations ± standard deviation.

iad of compounds present as identified by DHA/GC–MS. There were 85 individual compounds present in the raw seeds, and 65 of these were tentatively identified. The number of volatiles present in processed seeds were 117, 97, 93, and 87 in the R, RS, S, and M seeds, respectively, of which 87,67, 46, and 54 compounds were identified (see Tables 2–5). Classification of compounds present and their relative contribution to total volatiles for raw and processed seed pastes are discussed below.

Heterocyclics. Of the volatile compounds, pyrazines were the major compounds present in minute quantities, formed *via* Maillard reaction (16). Alkylpyrazines are generally recognized as having nutty and roasted aromas, and some elicit earthy or potato-like characteristics (17). While volatiles of RW sesame seed paste contained only small amounts of 2,5-dimethylpyrazine, roasted seeds contained 11 pyrazines. Meanwhile, only 2 volatile pyrazines were identified in the S and M sesame seed pastes, and 7 pyrazines were present in RS seeds (see Table 2).

The odor threshold values for mono-, di-, tri-, and tetramethylpyrazines are all relatively high (>1 ppm), and these compounds probably play a minor role in food aromas (18). However, replacing one or more of the methyl groups with ethyl moieties has a marked influence in lowering their threshold values, with some compounds possessing the roasted note of cooked foods (19). While 3 ethylpyrazines were present in the R seeds, RS seeds contained only one ethylpyrazine, namely 2-ethyl-5-methylpyrazine. The compound 2-acetyl-6-methylpyrazine, which is recognized as having a popcorn-like aroma with low threshold value in the ppb range, was present only in trace amounts in the roasted seeds. The relative content of pyrazines in sesame seed volatiles was 8.71% in R, 2.97% in RS, 2.04% in S and 0.53% in M, and only 0.25% in RW. The compound 2,5-dimethylpyrazine was the major contributor to the pyrazines in sesame seeds, while 2,6-dimethylpyrazine, present only in the RS seeds, might be formed from condensation of pyruvaldehyde with amino acids (1). Meanwhile, methylpyrazine, which was present in high amounts in R and RS seed pastes, was also found to contribute to the roasted aroma of clams (20). Park *et al.* (21) have recently reported the presence of 7 pyrazines in the volatiles of toasted sesame seed oil. However, Manley *et al.* (1) reported 24 pyrazines from roasted sesame seeds by using a steam distillation procedure. These authors also proposed different pathways for the formation of pyrazines from the condensation reactions of free amino acids and reducing sugars.

Pyrroles are found in the volatiles of most heated foods (22). There were 7 pyrroles present in the roasted sesame seeds, while only one pyrrole, namely 2-acetylpyrrole, was present in RW and all processed seeds in trace amounts. This compound possesses a desirable caramel-like aroma; however, alkylpyrroles might possess undesirable odors (17). The only other nitrogen-containing heterocyclic compound found in the aroma volatiles of sesame seeds was pyridine. This compound was present in the roasted seeds and is known to exert a pungent and unpleasant odor when present in foods (23). However, it has also been identified in fried chicken flavor (24).

Furans were the other group of heterocyclic compounds identified in the flavor volatiles of sesame seeds. Furan derivatives, such as furfural and furanones, occur in the volatiles

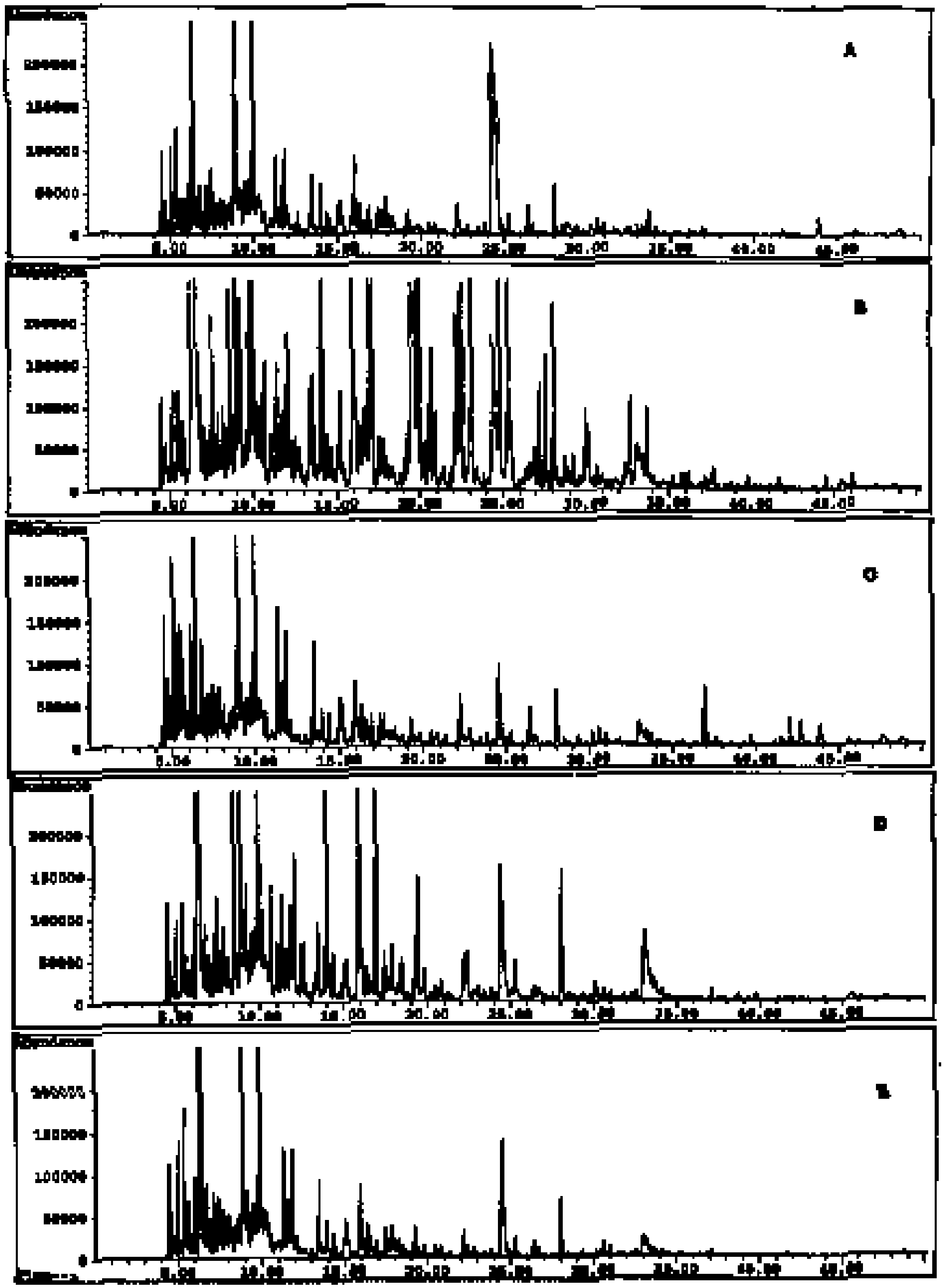

FIG. 1. Total ion chromatograms of volatiles of sesame seed pastes A, in the raw state; B, roasted; C, steamed; D, roasted plus steamed; and E, microwaved seeds.

TABLE 2
Heterocyclic Flavor Volatiles of Sesame Paste as RW, R, S, RS, and M Seeds[a]

Compound	RT (min)	RW	R	S	RS	M
Pyrazines						
2-Methylpyrazine	17.00	—	3.97	—	trace	trace
2,5-Dimethylpyrazine	19.32	0.25	4.40	0.27	1.28	0.32
2,6-Dimethylpyrazine	19.66	—	—	—	0.36	—
2,3-Dimethylpyrazine	20.49	—	0.44	—	0.18	—
2-Ethyl-3-methylpyrazine	22.13	—	0.69	—	—	—
2-Ethyl-5-methylpyrazine	22.40	—	1.16	—	0.60	—
2,3,5-Trimethylpyrazine	23.06	—	0.98	—	0.16	—
2,6-Dimethyl-3-ethylpyrazine	24.77	—	0.93	—	0.39	—
2-Ethyl-6-Methylpyrazine	26.59	—	0.08	—	—	—
2-Methyl-6-(1-propenyl)-pyrazine	26.81	—	0.20	—	—	—
3,5-Diethyl-2-methylpyrazine	28.73	—	0.06	—	—	—
2-Acetyl-6-methylpyrazine	35.18	—	trace	—	—	—
3-Methoxy-2,5-dimethylpyrazine	36.90	—	—	1.77	—	—
Pyrroles						
1-Ethyl-1H-pyrrole (?)	13.35	—	0.30	—	—	—
1-Methylpyrrole	21.85	—	0.05	—	—	—
Pyrrole	27.50	—	0.37	—	—	—
2-Methylpyrrole	29.15	—	0.07	—	—	—
2-Methylpyrrole	29.91	—	0.21	—	—	—
4-Ethyl-2-methylpyrrole	35.73	—	0.04	—	—	—
2-Acetylpyrrole	46.11	trace	trace	trace	trace	trace
Pyridines						
Pyridine	13.64	—	0.17	—	—	—
Furans						
3-Ethyl-2,5-dihydrofuran	4.79	—	0.11	1.00	0.12	—
2-Pentylfuran	15.12	0.70	0.24	0.90	0.22	0.66
2-Methyltetrahydrofuran-3-one	16.68	—	0.19	—	—	—
Furfural	25.22	0.51	0.86	0.31	0.31	0.58
2-Acetylfuran	27.15	—	0.31	—	—	—
5-Methylfurfural	30.07	—	0.18	—	—	—
Furfurylalcohol	33.63	0.67	1.19	0.31	0.31	0.09
Lactones						
Allylbutenolide	23.40	—	0.03	—	—	—
γ-Butyrolactone	32.60	trace	0.33	—	—	—

[a]Values given are percentage contribution to the total volatiles. RT: retention time; the sign "—" denotes not detected. See Table 1 for other abbreviations.

of all heated foods, are among the most abundant products of Maillard reactions, and possess a pleasant and sweet flavor note. Seven furans were identified in volatiles of processed sesame seeds, all of which were present in roasted seeds and contributed to 3.08% of its total volatiles. Oxygenated furans, such as furfural, 5-methylfurfural, and 2-acetylfuran, generally impart caramel-like, sweet, and fruity characteristics to foods (18,25). Compounds such as furfuryl alcohol are also believed to contribute to the roasted aroma of sesame seed oil (8). 2-Acetylfuran was present only in the volatiles of R and RS seeds. 2-Pentylfuran, a lipid oxidation product, which was present in the raw as well as all processed seed paste volatiles, was also present in the volatiles of roasted sesame seed oil as reported by Park *et al.* (21). Moreover, Schieberle (7,26,27) reported that 2-furfurylthiol, 4-hydroxy-2,5-dimethyl-3(2H)-furanone and 2-methyl-3[methyldithio]-furane were present in roasted sesame seeds and concluded that 2-furfurylthiol was the most important contributor to the roasted, caramel-like flavor note of moderately roasted sesame, along with 2-phenylethylthiol and 2-acetyl-1-pyrroline (7).

Carbonyl compounds. A maximum of 13 aldehydes was present in the volatile components of roasted sesame seeds, whereas 10, 8, 8, and 6 aldehydes were identified in the volatiles of RS, M, RW, and S seeds, respectively (Table 3). Higher proportions of aldehydes were present in the R and RS seeds (17.30 and 14.73%, respectively) as compared to M, S, and RW seeds. Both aerial- and enzyme-derived oxidation products of lipids were present in the pastes; however, the majority of aldehydes present was autoxidation products (28). The compound 2-methylbutanal with a fermented and fruity aroma was the dominant aldehyde present (29). However, 3-methylbutanal has been described as having a pungent and fruity flavor note (28). (*E*,*E*)-2,4-Decadienal was present at a much lower amount (0.04%) only in the roasted seeds and is known to contribute to the fried and oily character of the volatiles. Furthermore, (*E*)-2-butenal and 2-phenyl-2-butenal were present only in the roasted seed volatiles, but 4-methyl-2-pentenal and 2-hexenal were present in both R and RS seed volatiles.

The flavor character of aldehydes present in the volatiles

TABLE 3
Carbonyl Compounds in Flavor Volatiles of Sesame Paste from RW, R, S, RS, and M Seeds[a]

Compound	RT (min)	RW	R	S	RS	M
Aldehydes						
2-Methylbutanal	6.25	2.65	11.40	4.63	9.45	8.21
3-Methylbutanal	7.36	1.02	0.33	1.07	0.67	0.93
4-Methyl-2-pentenal	12.57	—	0.07	—	0.04	—
2-Hexenal	14.80	—	0.05	—	0.05	—
(*E*)-2-Butanal	15.60	—	0.26	—	—	—
Octanal	17.60	0.60	0.88	0.79	0.22	0.46
(*E*)-2-Heptenal	19.19	0.57	0.96	0.56	0.51	0.67
Nonanal	22.14	0.68	1.01	1.74	0.98	0.71
(*E*)-2-Octenal	23.79	0.14	0.08	0.27	0.11	0.13
Benzaldehyde	26.98	1.67	1.96	—	1.82	1.62
Phenylacetaldehyde	33.06	0.29	0.31	—	0.88	0.24
(*E,E*)-2,4-Decadienal	39.76	—	0.04	—	—	—
2-Phenyl-2-butenal	44.46	—	0.04	—	—	—
Ketones						
4-Methylcyclohexanone	5.69	—	—	—	—	0.30
2,3-Butanedione	7.19	0.77	0.70	0.39	0.46	0.71
Methyl-*tert*-butylketone	9.11	—	—	—	—	1.21
2,3-Pentanedione	9.16	—	0.49	00	1.42	00
Methylisoamylketone	13.31	0.34	—	—	—	—
2-Octanone	17.79	1.02	1.12	—	0.64	1.07
Acetoin	17.50	—	—	0.20	—	—
1-Octen-3-one	18.18	—	0.05	0.24	0.12	0.12
3-Hydroxy-2-pentanone	20.21	—	0.14	—	—	—
2-Cyclopenten-1-one	20.79	0.35	—	—	—	—
1-Hydroxy-3-methyl-2-butanone (?)	20.84	—	0.28	—	—	—
Acetophenone	33.41	trace	0.08	—	—	—

[a] Values given are percentage contribution to the total volatiles. The sign "—" denotes not detected. See Tables 1 and 2 for abbreviations.

of both RW and M sesame seed pastes was identical, both qualitatively and quantitatively, except for 2-methylbutanal, which was present at a 3-fold higher concentration in the M seeds as compared to the RW seed volatiles. Meanwhile, benzaldehyde and phenylacetaldehyde with distinct flavor notes were absent in S seed volatiles, and the concentrations of 2-methylbutanal and nonanal were higher in the S seeds as compared to the RW seeds.

Ketones, in general, are known to contribute to the sweet, floral, and fruity flavor of many foods (30). There were a total of 12 ketones present in all seed volatiles examined (Table 3). While 5 ketones were present in the volatiles of RW seeds, 7, 4, 5, and 5 ketones were detected in the aroma volatiles of R, S, RS, and M seed pastes, respectively. However, both the nature and content of ketones present depended heavily on the process employed. Nonetheless, volatiles of all processed seeds contained 2,3-butanedione (diacetyl), which is perceived as being the most important carbonyl compound contributing a buttery and meat-like aroma to foods (29). However, diacetyl is fairly unstable and may afford acetoin, which is present in all seed volatiles, except that of steamed seeds. The compounds 2,3-pentanedione, with a buttery flavor note similar to that of 2,3-butanedione, and 1-octen-3-one, with a desirable mushroom-like flavor note, were present in the volatiles of some processed seeds (29,31).

Hydrocarbons and alcohols. A variety of hydrocarbons were identified in the volatiles of RW sesame seeds (Table 4). Most importantly, from a toxicological viewpoint, aromatic hydrocarbons may be considered while some aliphatic hydrocarbons, such as alkanes, which are derived from oxidative decomposition of lipids, are believed to make no significant flavor contribution to foods (32). The aromatic hydrocarbons are presumably formed as by-products of sugar degradation (31). The threshold values of hydrocarbons are high, and therefore, they are not important as aroma compounds in foods (33). Even terpene hydrocarbons, which are quantitatively significant in essential oils, possess little flavor value. However, terpenes convey a definite "freshness" to the odor profile (34).

Similarly, alcohols are generally considered as minor contributors to flavor, unless present in a relatively high concentration or bearing unsaturation sites. There were a total of 10 alcohols present in the volatiles of different sesame seeds (Table 4); 7 alcohols were present in the volatiles of R, S, RS, and M seeds. The alcohols present in the RW sesame seed volatiles, but absent in the processed seeds, were *n*-pentanol, *n*-octanol, ethylene glycol monobutyl ether, 2,3-butanediol, and 2-pentylethanol. *n*-Butanol was also present in the volatiles of S sesame seeds. The only alcohol present in the aroma volatiles of all sesame seeds was 2-ethylhexanol.

The compound 3-methyl-1-butanol (isopentanol) was identified in the volatiles of R and M seeds and is known to play an important role in the flavor volatiles of fermented

TABLE 4
Hydrocarbons, and Alcohols in Flavor Volatiles of Sesame Paste as RW, R, S, RS, and M Seeds[a]

Compound	RT (min)	RW	R	S	RS	M
Hydrocarbons						
n-Heptane	4.42	0.93	0.10	1.34	0.40	0.98
2-Heptene	4.60	0.46	0.09	0.86	0.19	0.56
Methyl-1,3-pentadiene	4.66	0.20	—	—	—	0.26
n-Octane	4.98	1.03	0.37	2.42	0.51	1.32
2-Octene	5.60	—	trace	—	0.34	0.80
n-Nonane	5.98	0.75	0.04	1.94	0.39	1.27
1-Methyl-2-pentylcyclopropane	6.61	0.52	—	1.58	—	—
Benzene	6.72	0.87	0.17	1.46	0.44	1.19
2,5-Heptadiene	6.92	—	0.05	—	—	—
2,2-Dimethyldecane (?)	7.55	0.84	—	—	—	—
n-Decane	7.73	0.50	0.13	0.94	0.44	0.81
α-Pinene	8.40	0.53	0.46	0.86	1.62	trace
Toluene	8.84	6.60	1.12	8.91	3.54	6.81
3,6-Dimethyldecane	9.06	0.83	—	—	—	0.08
3,7-Dimethylundecane	9.38	—	—	—	0.15	—
Camphene	9.51	—	—	—	0.61	—
n-Undecane	10.08	—	1.24	0.70	0.56	—
5-Propylnonane	10.16	—	—	—	0.28	—
β-Pinene	10.59	0.51	0.31	0.63	0.94	0.61
Sabinene	11.02	—	0.14	—	0.47	—
Ethylbenzene	11.27	1.76	0.36	2.77	0.89	2.56
p-Xylene	11.55	0.99	0.19	1.18	0.48	1.30
m-Xylene	11.84	2.21	0.37	2.11	0.87	2.58
Carene	12.05	—	0.38	—	—	—
Myrcene	12.45	—	0.12	—	0.42	—
α-Phallandrene	12.60	0.44	0.12	—	0.49	—
α-Terpinene	13.20	—	0.06	—	0.10	00
o-Xylene	13.42	1.75	0.29	2.86	0.72	2.11
Limonene	13.94	1.29	0.84	0.84	2.92	0.60
Propylbenzene (?)	14.36	0.49	0.18	0.68	0.37	0.53
1-Ethyl-4-methylbenzene	14.89	0.58	—	0.36	—	0.22
Ethyltoluene	14.98	0.21	0.15	0.92	0.08	0.72
(*Z*)-Ocimene	15.24	0.38	—	—	—	—
(*E*)-Ocimene	15.95	2.64	9.31	0.96	4.30	1.57
Styrene	16.31	0.68	0.15	0.92	0.27	0.71
1-Ethyl-3-methylbenzene	16.52	0.29	—	0.46	0.22	0.42
p-Cynane	16.84	0.73	00	0.62	2.10	0.31
1,3,5-Trimethylbenzene	17.36	0.87	0.20	0.75	0.68	0.67
4-Ethyl-1,2-dimeethylbenzene (?)	21.07	trace	—	—	—	0.33
α-Cubebene	26.68	0.16	—	—	—	0.15
n-Hexadecane	30.98	0.40	—	—	—	0.23
Naphthalene	37.10	trace	—	—	0.11	—
Alcohols						
n-Butanol (?)	12.02	0.33	—	0.41	—	—
n-Pentanol	14.21	0.08	—	—	—	—
Isopentanol	16.09	—	0.25	—	—	0.60
1-Octen-3-ol	18.45	—	0.68	—	0.37	0.25
n-Hexanol	20.74	—	0.05	0.16	—	—
n-Octanol	21.14	0.11	—	—	—	—
Ethyleneglycol monobutyl ether	22.76	0.36	—	—	—	—
2-Ethylhexanol	26.36	0.98	1.88	1.34	1.58	0.58
2,3-Butanediol	28.77	0.33	—	—	—	—
2-Phenylethanol	47.78	0.79	—	—	—	—

[a]Values given are percentage contribution to the total volatiles. The sign "—" denotes not detected. See Tables 1 and 2 for abbreviations.

shellfish products (35). Meanwhile, 1-octen-3-ol, present in the aroma volatiles of R, S and M seeds, is well-known to impart a desirable mushroom-like aroma to products (36) and is a character impact compound of mushroom (31).

Other compounds. Table 5 summarizes the flavor volatiles of sesame seed pastes belonging to carboxylic acid, ester, phenol, and sulfide groups. Acetic acid, with a vinegar-like and acidic aroma, was present in all seeds and was a major

TABLE 5
Acids, Esters, Phenols, and Sulfides in Flavor Volatiles of Sesame Paste in the RW, R, S, RS, and M Seeds[a]

Compound	RT (min)	RW	R	S	RS	M
Acids						
Acetic acid	24.39	18.32	0.52	3.36	2.82	6.57
Butyric acid	32.26	—	0.06	—	—	—
Hexanoic acid	41.12	trace	trace	trace	trace	trace
Esters						
Ethyl acetate	5.80	0.54	trace	0.52	0.17	0.39
Ethyl decanoate (?)	7.10	trace	—	—	—	—
Phenols						
Guaiacol	41.68	trace	trace	—	—	—
Phenol	47.58	trace	—	—	—	—
4-Ethylguaiacol	48.79	trace	—	—	—	—
Sulfides						
Dimethylsulfide	4.71	—	0.08	—	trace	—
Dimethyldisulfide	9.76	—	1.32	—	trace	—

[a] Values given are percentage contribution to the total volatiles. The sign "—" denotes not detected. See Tables 1 and 2 for abbreviations.

contributor to the aroma of RW sesame seeds. Its concentration was diminished markedly in processed seeds, especially in R and RS seeds. However, hexanoic acid was present in trace amounts in all seed volatiles, and butyric acid was only detected in the aroma constituents of roasted seeds.

There were two esters present in sesame seed volatiles. Ethyl acetate, with a pleasant ripening fruit aroma, was present in volatiles of both RW and processed sesame seeds, while ethyl decanoate was present in trace amounts only in the RW seeds (Table 5). Three phenols were also present in trace amounts in the RW sesame seeds, and guaiacol was also present in the R seed volatiles. Both guaiacol and phenol are known to possess sweet and phenolic aroma notes, while 4-ethylguaiacol has a clove-like odor (18). Schieberle (26) has also reported the presence of 2-methoxyphenol and 4-vinyl-2-methoxyphenol in the aroma volatiles of roasted black and white sesame seeds. These latter compounds are formed *via* degradation of natural phenolics of sesame seeds (1).

Two sulfides, namely dimethylsulfide and dimethyl disulfide, were present only in the roasted seeds (Table 5). The latter compound may be formed from oxidation coupling of methanethiol (37). Schieberle (26) has reported the presence of several sulfur-containing compounds as key aroma compounds in black and white sesame seeds. Presence of sulfur compounds in the aroma volatiles of cooked products is common, and these are known to contribute to both pleasant and unpleasant flavor characteristics of foods (38).

Multivariate analysis. The relationships among the five sesame samples were clearly indicated on the basis of factors 1 and 2, as shown in Figure 2. RW and M samples seem to possess almost the same characteristics because they overlapped each other in the factor score plot (Fig. 2). Similarly, the odor of R, RS, and S sesame may be well acceptable if we consider other information on the samples. However, the latter did not possess the desired flavor as evidenced by its sensory characteristics.

Table 6 summarizes factor loadings, eigenvalues, and cumulative properties of extracted factors 1, 2, and 3. All amino acids correlated highly positively to Factor 1. On the contrary, many pyrazines and some terpines loaded negatively on factor 1.

As clearly indicated by overlapping with the raw sample (Fig. 2), the large factor 1 score of the M sample indicates that the changes in components caused by microwave treatment were relatively small. However, highly negative scores indicate loss of large amounts of free amino acids in R and RS samples and production of large amounts of volatiles in these samples. Interpretation of factor 2 was different, but meanings contained in factor 3 can be interpreted as follows. Original seed components, such as pinenes, myrcene and sabinene, loaded positively on factor 3, but compounds produced by different heat treatments, such as furfural, octanal and (*E*)-2-octenal, were negatively loaded. Thus, factor 3 implies the contrast between volatile components originally contained in seeds and those produced by heat treatment.

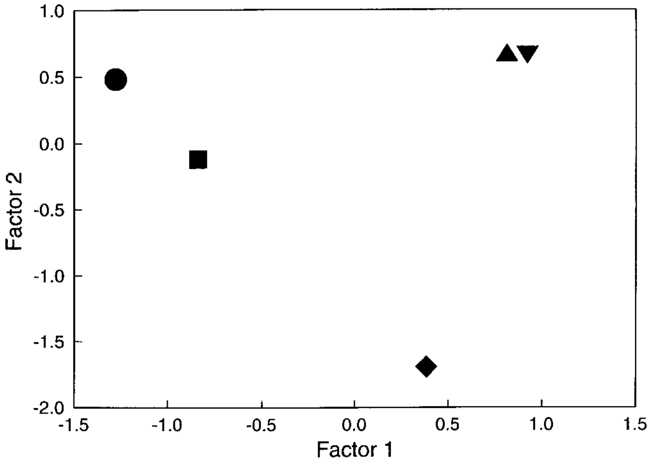

FIG. 2. Factor score plot of sesame seed samples. Symbols are: ▼, raw; ▲, microwave; ◆, steamed; ■, roasted-steamed; and ●, roasted.

TABLE 6
Factor Analysis of Combined Volatiles, and Amino Acids Data[a]

Compound	Factor 1	Factor 2	Factor 3
1,3,5-Trimethylbenzene	0.76929		
2,3,5-Trimethylpyrazine	–0.81400		
2,3-Butanedione		0.89864	
2,3-Dimethylpyrazine	–0.92409		
2,3-Pentanedione	–0.73612		
2,3-Dimethylpyrazine	–0.85447		
3,6-Dimethyldecane			
2,6-Dimethyl-3-ethylpyrazine	–0.92738		
3-Ethyl-2,5-dihydrofuran		–0.97182	
1-Ethyl-3-methylbenzene	0.83873		
1-Ethyl-4-methylbenzene	0.82055		
2-Ethyl-5-methylpyrazine	–0.95329		
2-Ethylhexanol	–0.92784		
2-Heptene	0.77027		
2-Hexenal	–0.96691		
1-Methyl-2-pentylcyclopropane		–0.84536	
4-Methyl-2-pentenal	–0.96351		
3-Methylbutanal	0.90694		
2-Methylbutanal	–0.77115		
2-Octanone		0.98547	
1-Octen-3-ol	–0.83432		
1-Octen-3-one		–0.87910	
2-Octene			
2-Pentylfuran	0.85654		
α-Phellandrene			0.73823
α-Terpinene	–0.87257		
Acetic acid			
Benzaldehyde		0.90877	
Benzene	0.84073		
Butanol			
Cubebene	0.79069		
Cymene		0.95882	
Decane	0.76320		
(*E*)-2-Heptenal			–0.76648
(*E*)-2-Octenal		–0.86202	
(*E*)-Ocimene	–0.86092		
Ethylacetate	0.91552		
Ethylbenzene	0.87498		
Ethyltoluene			
Furfural			–0.70223
Furfuryl alcohol			
n-Hexadecane	0.73632		
Hexanol		–0.88794	
Iso-pentanol			
Limonene			0.89352
Methyl-1,3-pentadiene	0.78826		
m-Xylene	0.99165		
Myrcene			0.70999
n-Heptane	0.86370		
Nonanal		–0.96547	
Nonane	0.71628		
o-Xylene	0.83626		
Octanal			–0.92494
Octane		–0.73874	
Phenylaldehyde			0.79415
α-Pinene			0.71468
β-Pinene			0.91222
Propylbenzene	0.80977		
p-Xylene	0.95310		
Sabinene	–0.70397		0.70153
Styrene	0.88277		
Toluene	0.86927		
Alanine	0.83230		

(continued)

TABLE 6 (continued)

Compound	Factor 1	Factor 2	Factor 3
γ-Aminobutyric acid	0.79595		
Arginine	0.87258		
Asparagine	0.84149		
Aspartic acid	0.86154		
Cysteine	0.88861		
Glutamic acid	0.84393		
Glutamine	0.89413		
Glycine	0.76879		
Histidine	0.88211		
Isoleucine	0.92751		
Proline	0.90512		
Leucine	0.88950		
Lysine	0.85697		
Methionine	0.83166		
Phenylalanine	0.84388		
Serine	0.86488		
Tryptophan	0.82673		
Threonine	0.93059		
Tyrosine	0.88171		

[a]Eigenvalue and cumulative proportion (%) of factor 1, factor 2, and factor 3 were 46.4, 55.2; 21.2, 80.5; and 10.7, 93.2, respectively.

Figure 3 shows the cluster analysis of amino acids, volatiles, and their combination. Relationships among samples were almost similar to those shown in the factor plot (Fig. 2). All clusters clearly show the similarity between RW and M as well as between R and RS samples. However, S samples behaved somewhat differently from the other four samples.

CONCLUSION

In conclusion, the content of free amino acids in sesame seed pastes depended largely on the processing conditions employed; R and RS were most effective in reducing the content of free amino acids, presumably *via* condensation with reducing sugars present in the seeds. Heterocyclic compounds,

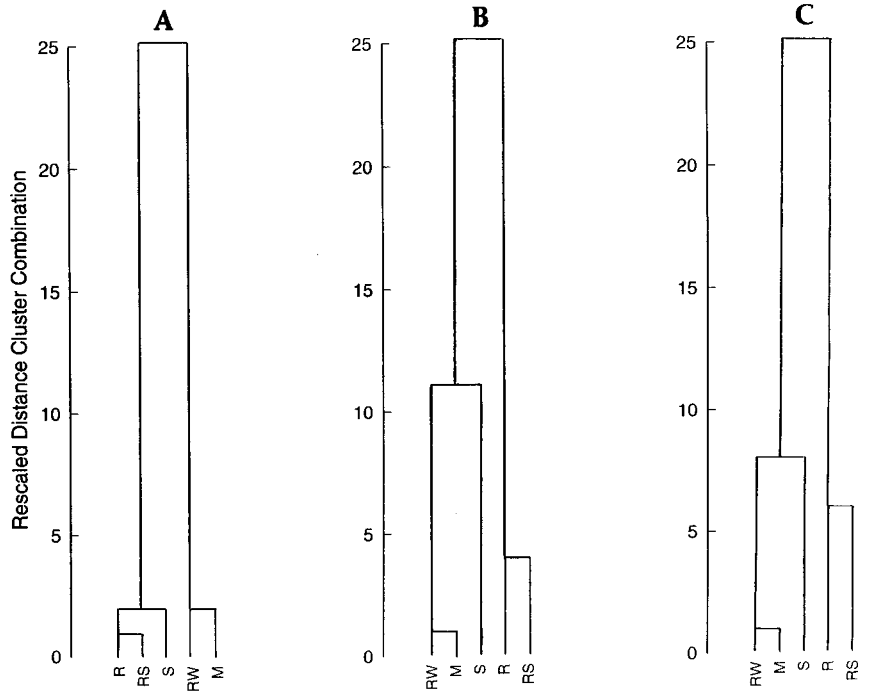

FIG. 3. Cluster analysis of free amino acids, volatiles, and their combined data. A, free amino acids; B, flavor volatiles; C, free amino acids and flavor volatiles. RW, raw; M, microwaved; S, steamed; R, roasted; and RS, roasted plus steamed.

mainly pyrazines, furans and pyrroles, were the main contributors to the aroma of roasted sesame seeds. Production of flavor-active volatiles in R and RS samples was negatively correlated with depletion of free amino acids in the samples. The aroma volatiles of R and M seeds were quite similar and they closely resembled volatiles from S seeds. Thus, R is essential to the development of character-impact flavor volatiles in sesame seeds. However, controlled S may be employed to modify the flavor of R seeds as might be desired in specific applications (38).

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